Online Resource 2

Computational methods and reproducibility record

Spectral overlap and molecular sampling in Raman enhancement at nanoparticle oxide metal interfaces

Journal: Plasmonics
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This PDF is the readable companion to ESM_2.zip. It documents the executed model, retained numerical results, field reconstruction and reproduction procedure. The ZIP supplies the executable code, material tables and machine-readable complex fields; the PDF does not replace those files. Analytical derivations and additional tables and figures are provided in Online Resource 1.

1 Model and sampling conventions

Quantity	Prescribed input
Particles	Two gold spheres; radius 60 nm
Support	Aluminium half-space with a planar nonabsorbing oxide, n = 1.65
Nominal geometry	Oxide t = 3 nm; minimum air spacer s = 5 nm; surface gap g = 20 nm
Sphere centres	(±(60 + g/2), 0, 60 + t + s) nm
Reporters	Inward/outward positions relative to left centre: (+61, 0, 0) and (-61, 0, 0) nm
Illumination and detection	Pump and reciprocal incidence along -z, x polarized; detection along +z, x polarized
Molecular response	x-directed rank-one Raman tensor; equal reporter weights 1/2, 1/2
Raman shift and reference	1580 cm^-1; incoming electric-field amplitude 1; homogeneous-air kernel 1

Gold optical constants use Johnson and Christy [2]; aluminium uses the tabulated Rakić Lorentz-Drude model [3]. Interpolation is linear in vacuum wavelength for n and k, with no extrapolation. The retained datasets and checksums identify the exact inputs. The full-wave implementation uses SMUTHI 2.2.4 [1].

At pump wavelength λ_L in nm, $\lambda_S = 10^7 / (10^7/\lambda_L - 1580)$. Each frequency is solved independently. At site i, $G_{L,i} = |E_{x,L,i}|^2$, $G_{S,i} = |E_{x,S,i}|^2$ and $K_i = G_{L,i}G_{S,i}$. The reported mean is $(K_1 + K_2)/2$.

2 Wavelength and geometry results

The primary design contains 213 pump/Stokes pairs. The nominal geometry and both endpoints of each one-factor sweep have spectra from 500 to 900 nm on a 25 nm coarse grid, with 633 and 785 nm added. Five-nanometre local refinement surrounds the seven Raman maxima and the nominal pump-only and scattering maxima. Interior geometry levels are evaluated at 633 and 785 nm.

Factor	Five levels (nm)	Nominal (nm)	Central step (nm)
Oxide t	1, 2, 3, 4, 5	3	1
Air spacer s	3, 4, 5, 6, 7	5	1
Gap g	10, 15, 20, 25, 30	20	5

At the nominal geometry, the sampled mean-kernel maximum is at **595 nm** (278596.620946). The pump-only mean $|E_{x,L}|^4$ peaks at **680 nm**; the upward particle-scattering cross-section peaks at **580 nm**. Choosing these alternative wavelengths yields 55.41% and 88.43%, respectively, of the largest sampled mean Raman kernel.

t (nm)	s (nm)	g (nm)	Sampled peak (nm)	Maximum mean K
3	5	20	595	278597
1	5	20	595	252355
5	5	20	595	299860
3	3	20	605	178931
3	7	20	595	355621
3	5	10	670	3.26925e+06
3	5	30	585	89677.7

Normalized finite sensitivity is $S_d = [d_0/K_{mean}(d_0)]\,[K_{mean}(d_0 + \Delta d) - K_{mean}(d_0 - \Delta d)]/(2\Delta d)$. The response span is the maximum divided by the minimum over the five tested levels. These are finite-step model comparisons, not confidence intervals.

Factor	Pump (nm)	Sensitivity	Maximum/minimum span
Oxide	633	0.191730	1.291760
Oxide	785	0.130686	1.189940
Spacer	633	0.855589	1.951797
Spacer	785	-0.061164	1.065963
Gap	633	-4.909221	54.408419
Gap	785	-5.062732	63.879402

3 Numerical verification

All 13 geometries were checked at 633 and 785 nm. The seven spectral geometries were also checked at their refined Raman maxima. Forty retained paired checks include these mandatory points and earlier coarse-maximum checks. All passed the 0.5% target for tested projected intensities, individual site kernels and mean kernels. The archive contains 510 frequency solutions: 426 primary, 80 refinement and four pilot solutions.

Setting	Primary	Refinement check
Multipole cutoff lmax = mmax	20	24
Effective-index truncation	50	70
Maximum contour step	0.02	0.01
Imaginary contour depth	0.10	0.15
Local-field azimuthal intervals	96	192
Reflected local fields	Double precision	Double precision

The contour passes through 0, 0.8, 0.8 - iδ, 3.5 - iδ, 3.5 and the truncation value. A diagonal similarity transformation improves the numerical scaling of the same Maxwell system. The vectorized top-layer Sommerfeld coupling is not a dipole or stationary-phase approximation.

t/s/g (nm)	Max intensity change (%)	Max site K change (%)	Mean K change (%)
1/5/20	0.00961	0.01703	0.01681
2/5/20	0.00740	0.01194	0.01185
3/3/20	0.01757	0.02642	0.01198
3/4/20	0.00564	0.00903	0.00891
3/5/10	0.06573	0.11752	0.11751
3/5/15	0.00772	0.01418	0.01414
3/5/20	0.01063	0.01806	0.01793
3/5/25	0.00980	0.01529	0.01510
3/5/30	0.01276	0.02359	0.02293
3/6/20	0.01005	0.01541	0.01534
3/7/20	0.01157	0.01850	0.01847
4/5/20	0.00850	0.01380	0.01372
5/5/20	0.01116	0.01864	0.01855

The largest relative linear-system residual is 2.95e-15. An independent multilayer Fresnel calculation reproduces the retained background fields to maximum relative difference 1.68e-07. The upstream/vectorized coupling comparison gives relative matrix error 1.07×10^{-11} and maximum four-frequency projected-intensity difference 1.36×10^{-8}.

Doubling the scattering angular grid from 61 × 97 to 121 × 193 nodes changes the upward cross-section by at most 0.0158649% at the tested pumps 580, 595, 633, 680 and 785 nm. Upward scattering excludes the bare-support reflected plane wave; it is not extinction or total reflectance.

4 Complex fields and reconstruction

The following baseline x components are extracted directly from the retained primary NPZ files. Fields are complex and normalized to unit incident amplitude. The reporters remain registered between pump and Stokes calculations. Full Cartesian total, background and scattered fields, coordinates, optical constants, multipole coefficients and integration contours remain in the ZIP.

Wavelength (nm)	Site	Re Ex	Im Ex	Gx = |Ex|²
633.000000	Inward	-23.31666	5.286301	571.6118
633.000000	Outward	-6.340406	6.624165	84.0803
703.344274	Inward	-18.3667	19.56867	720.2687
703.344274	Outward	-4.178934	7.089923	67.7305
785.000000	Inward	-6.386559	15.85052	292.027
785.000000	Outward	-1.895577	5.906248	38.47698
896.149412	Inward	-3.112943	11.69502	146.4639
896.149412	Outward	-1.113101	4.755964	23.85819

Pump (nm)	Site	GL	GS	Site K
633	Inward	571.612	720.269	411714
633	Outward	84.0803	67.7305	5694.8
785	Inward	292.027	146.464	42771.4
785	Outward	38.477	23.8582	917.991

The nominal primary mean kernels are 208704.441676 at 633 nm and 21844.703877 at 785 nm. The separately averaged products underestimate these means by 38.1081% and 35.5769%. These are means over two equally weighted prescribed sites, not integrals over an experimentally measured particle surface.

Retained array conventions

In each field NPZ, total_E, background_E and scattered_E have shape (3, 2): Cartesian component on the first axis and inward/outward reporter on the second. xyz_nm has shape (2, 3); coefficients has one row per particle. Wavelength, geometry and quadrature settings are retained. Loading uses numpy.load without pickle. Adjacent JSON files contain projected intensities and residuals.

The analysis checks total_E = background_E + scattered_E, reconstructs Gx from the complex x component, and verifies that both reporters remain 61 nm from the left-particle centre. Paired JSON and CSV records retain both frequencies and their site registration, allowing mean products and finite differences to be recalculated without inferring missing fields.

5 Reproduction and file map

Use a separate Python 3.12 environment and the supplied dependency files. Run commands from the extracted ESM_2 directory. Optional compilation uses Linux/GCC, OpenMP and the listed Cython dependencies; the upstream pure-Python direct translations remain available with a substantial runtime penalty.

```
python -m pip install -r requirements-tested.txt
python -m pip install -r requirements-optional-acceleration.txt
python scripts/build_optional_acceleration.py
python scripts/run_parameter_study.py --phase scan
python scripts/run_parameter_study.py --phase refine
python scripts/run_parameter_study.py --phase check
python scripts/analyze_parameter_study.py
python scripts/check_parameter_archive.py
python scripts/check_scattering_quadrature.py
```

Path in ESM_2.zip	Contents
parameter_study/fields/	Complex fields, coefficients and per-frequency metadata
parameter_study/pair_scan_*.json	Registered primary pump/Stokes pairs
parameter_study/pair_check_*.json	Paired numerical refinements
parameter_study/summary.json	Spectral maxima, sensitivities and verification summary
parameter_study/*.csv	Derived numerical values and complex field components
results/	Original fixed-geometry benchmark and its convergence records
materials/ and vendor/	Exact optical datasets and retained SMUTHI source
scripts/ and SHA256SUMS.txt	Executable analysis and simulation code; file integrity hashes

Completed records are cached by geometry, numerical settings and wavelength. Execute phases sequentially. A clean rerun reproduces the mandatory final coverage of 33 paired checks; the archived 40 additionally include seven earlier coarse-maximum checks. The selected fixed-geometry benchmark uses separately tested settings and is distinguished explicitly from the extended scan.

Interpretation limits

The geometry sweeps vary one factor at a time and do not determine interactions or a global optimum. Peak wavelengths are sampled maxima with 5 nm local spacing. Numerical self-consistency does not establish material-input accuracy, experimental validation, adsorption distributions, chemical enhancement or detection limits. Instrumental throughput, molecular dispersion and the Stokes-frequency photon factor can shift the wavelength maximizing measured counts.

References

[1] Egel A et al (2021) SMUTHI: a Python package for the simulation of light scattering by multiple particles near or between planar interfaces. J Quant Spectrosc Radiat Transf 273:107846. https://doi.org/10.1016/j.jqsrt.2021.107846

[2] Johnson PB, Christy RW (1972) Optical constants of the noble metals. Phys Rev B 6:4370-4379. https://doi.org/10.1103/PhysRevB.6.4370

[3] Rakić AD et al (1998) Optical properties of metallic films for vertical-cavity optoelectronic devices. Appl Opt 37:5271-5283. https://doi.org/10.1364/AO.37.005271